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(56) Documents Cited
US 5216536 A
Patent Abstracts of Japan P-939 Vol.13 No. 438 page 119 & JP1167735 WPI Abstract Accession No.86-322535/49 & JP61239227 WPI Abstract Accession No.86-322531/49 & JP61239223

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(54) Electrochromic display

(57) A variable reflectivity mirror comprises, in order under protective glass:
(1) a layer of fluorine-doped tin oxide conductor
(2) an electrochromic transparent layer of WO_3, which goes blue when hydrogen is introduced;
(3) a porous layer of SiO_2/Al_2O_3 which becomes moist on exposure to humidity; and
(4) a layer of reflective metal, e.g. silver, porous enough to allow access of water vapour to the layer (3).
The mirror's reflectivity is varied by applying an appropriate potential between the layers (1) and (4).

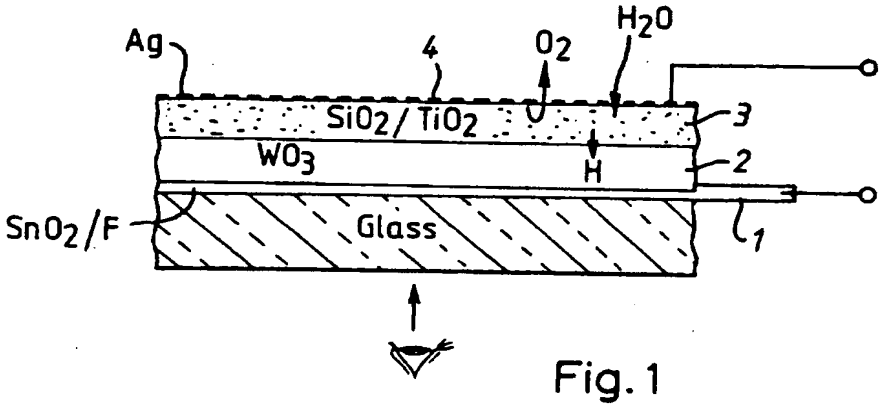


Fig. 1

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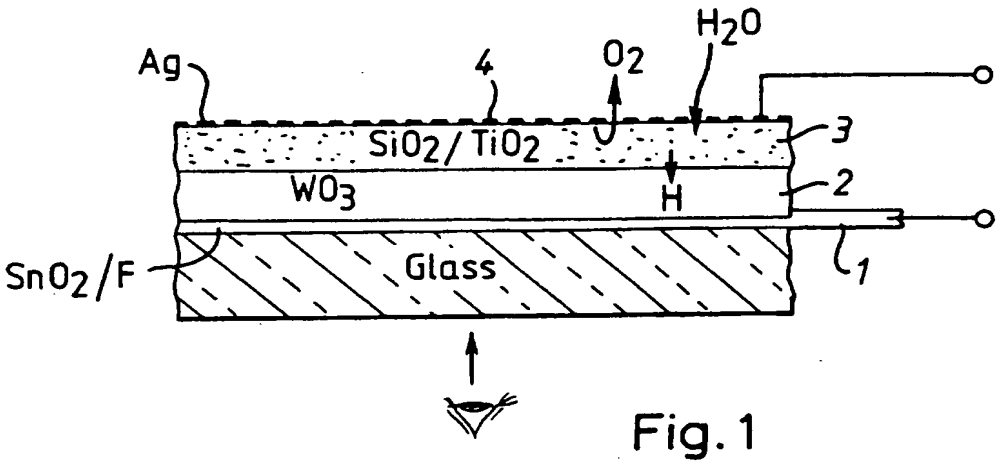


Fig. 1

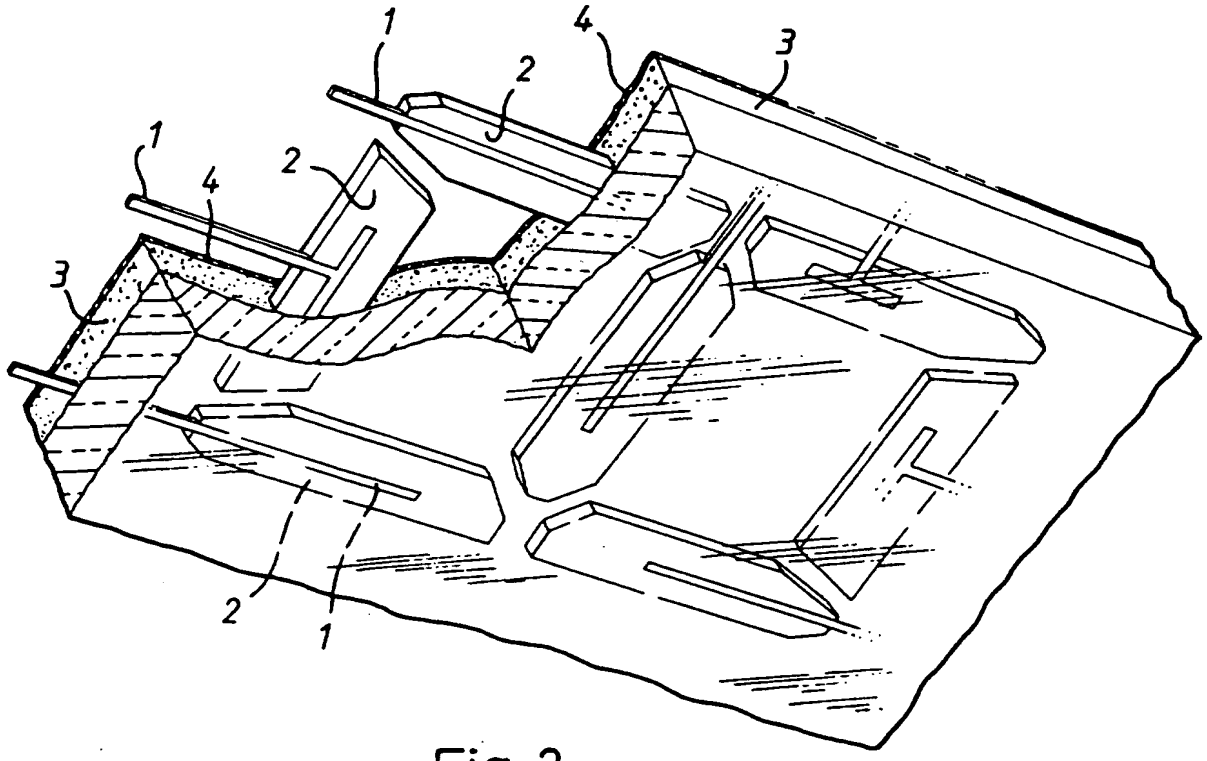


Fig. 2

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ELECTROCHROMIC DISPLAY DEVICE

This invention relates to an electrochromic display device requiring no guest metal to achieve a change in state of the display. The need to provide not only a supply of guest metal (lithium is commonly used) but also a reservoir for storing the guest metal has imposed severe design constraints on electrochromic displays and has also imposed the need for a high standard of hermetic sealing of the devices.

A typical electrochromic display device is described in UK Patent GB 2081922B. The device comprises the following layers (starting with the nearest to the viewer):

(i) an indium-tin-oxide conductive window;

(ii) tungsten trioxide (which goes from colourless to blue as lithium ions are incorporated);

(iii) a conductor for lithium ions (e.g. Li-β-alumina) incorporating a white opacifier such as TiO_2 powder;

(iv) a reservoir for lithium ions (e.g. $Li_{0.2}\ WO_3$); and

(v) a planar electronically conductive layer.

The device is activated by applying an appropriate potential between (i) and (v) to move lithium ions into or out of (ii).

Because (iii) and (iv) are opaque, this device cannot be used as a window or mirror without further modification. Suitable modifications to make an electrochromic window have been described in UK Patent GB 2164170B. The conductor (iii) may be "Bordeaux glass", consisting of LiCl, Li_2O and B_2O_3. The reservoir (iv) may be deposited as small islands of a host material for lithium such as a solid solution of MoO_3 and V_2O_5, with the space between the islands occupied by a transparent insulator such as SiO_2 or MgF_2, whereby the layer including (iv), viewed with the resolution achievable by the human eye, appears transparent. On applying a potential between (i) and (iv), the layer (ii) varies from coloured to transparent while the layer (iv) varies in the same direction, or not at all, or in opposition to (ii) but at a lesser rate, whereby an overall darkening/lightening of the structure occurs.

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That patent states that in other systems proposed previously, hydrogen is used as the guest atom and is derived by electrolysis in the cell of traces of water adsorbed on the surface of the tungsten trioxide from the air. Such systems, it was said, are unlikely to be sufficiently durable for use as windows, which can reach very high temperatures in the sun, particularly as water can corrode tungsten oxide layers in the presence of the high fields used in such systems.

According to the present invention, an electrochromic display device comprises, in order:

(1) a layer of a transparent electrically conductive material;

(2) a layer of an electrochromic material which changes colour when atoms resulting from electrolysis of water are dissolved in it;

(3) a layer which acts as a source of water; and

(4) a layer of a reflecting electronic conductor,

characterised in that the layer (3) is of an insulating transparent material having interconnected pores which are such that they spontaneously become moist on exposure to humidity, and further characterised in that the layer (4) is sufficiently porous to allow access of water vapour to the layer (3).

In use, the device is coloured/uncoloured by applying a potential between the layers (1) and (4).

Preferably the layer (4) is porous metal, preferably a reflective metal such as silver, chromium or aluminium.

The layer (3) may be an insulating oxide (such as a mixed oxide) formed by drying a sol gel, e.g. to yield SiO_2, TiO_2, SiO_2/TiO_2 or Al_2O_3, in a layer preferably from 0.2 to 1 micron thick, and may be transparent or may be dyed. The pores in the layer (3) may be 3-50Å across, typically from 0.5 to 3 nm across.

The layer 1 preferably has a sheet resistance of 5 to 500 ohms per square, more preferably 10 to 50 ohms per square.

The layer 2 may typically be 0.1 to 1 micron thick.

The invention will now be described by way of example with reference to the accompanying drawings, in which:-

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Figure 1 is a schematic cross-section of a device according to the invention, and Figure 2 is a schematic partly sectioned perspective view of a device with a display pattern, according to the invention. In both Figures, the device is drawn so as to be intended to be viewed from above.

Turning to Figure 1, which shows a variable interior rear-view car mirror, a transparent substrate of glass (or plastic could be used in certain circumstances, e.g. when high temperature heat treatment was not employed) carries underneath a transparent electronically conducting coating 1 such as fluorine doped tin oxide. The coating 1 has a sheet resistance of about 18 ohms per square, and is connected via a contact and wire to an external control circuit (not shown). Underneath this is a 0.2 micron film 2 of stoichiometric tungsten trioxide or other electrochromic oxide material one-third of a micron thick. Tungsten trioxide is colourless as a pure host material, and blue when hydrogen atoms are inserted.

Underneath this is a porous layer 3 some 0.3 microns thick of insulating and transparent inert material such as silica, titania, silica/titania or alumina, which is of an interconnected pore size distribution such that it spontaneously fills with water on exposure to ordinarily humid (RH > 10%) air and can thus act as a source of water. The material is made by the standard sol/gel techniques described in SPIE Vol. 1328 (1990) 352-362, which discloses that just such a pore size distribution (0.5 - 3 nm) results. Instead of a sol gel route, other thin film deposition methods leading to microporous structures might be used, such as rapid thermal deposition in the presence of excess inert gas, or chemical vapour deposition processes. After deposition, the layer 3 may be baked at up to 400°C, e.g. at 300°C, to remove unwanted organic matter.

On the underside of the layer 3 is deposited by vapour technique a thin porous film 4 of metal which performs several functions. Connected via pad and lead to the external control circuit mentioned earlier, it is the counter electrode of the low-field electrochemical cell made up of 1-2-3-4. It is furthermore an optical reflector, which can provide an essential part of the mirror or display function. It is important that the metal film 4 does not seal off all the pores of the water-source porous layer 3. To this end the metal is evaporated from a small-area source at a very acute angle to the surface of the

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layer 3; also the metal is of a kind which at the substrate deposition temperature gives a non-conformal deposit, i.e. the evaporated metal atoms have no mobility over the surface of layer 3 and hence have no propensity to 'self-heal' the gaps in the film 4. Chromium metal or aluminium or silver at reduced substrate temperature will fulfil these requirements, and in this example silver was used. Silver offers the best reflectivity (98%), while aluminium is very good (92%) and, in special circumstances, chromium (70%) may be used.

In use, the cell 1-2-3-4 would behave as follows. At relative humidity greater than about 10% a substantial volume of the interconnected pore structure of the porous layer 3 would be filled with adsorbed water derived from the atmosphere and furthermore this water is saturated with carbon dioxide from the air giving rise to a weakly acid solution of approximately 1.3 MΩ.cm resistivity. On application of a "write" voltage from the external circuit (potential on 1 is negative relative to 4), a current will flow across the cell electrolysing the water in 3, and discharging hydrogen into the tungsten trioxide WO_3 of layer 2. The hydrogen dissolves in the WO_3 to give a blue tungsten bronze, this being the electrochromic reaction as already described. The mirror is thus dulled to whatever degree is required. At the same time as this reaction, oxygen will be discharged at the porous metal electrode 4 and will vent to the atmosphere. Reversal of the potential, i.e. application of an "erase" voltage, will extract the hydrogen from the WO_3 into the layer 3 to form water and at the same time will discharge hydrogen at the metal electrode 4, which hydrogen will be vented to the atmosphere. In the case of silver as the electrode 4, this hydrogen has the beneficial effect that any corrosion product formed on the silver, notably silver sulphide, will tend to be reduced back to metallic silver.

Turning now to Figure 2, the device which has been described in relation to Figure 1 can be modified so that specified areas only are addressed. The Figure 2 device can be a mirror giving topical information (e.g. a price on a supermarket shelf) in an attractive form, in this case in blue figures on a shiny or bright (specular) background, legible even at acute angles of view. The same reference numerals apply to the same layers in both Figures. Thus, layers 1 and 2, of Figure 1, might be structured in the manner shown on Figure 2, while the glass and the layer 3 and metal film 4 remain, as in Figure 1,

large-area continuous planes. The tin oxide 1 is patterned to give a set of conductive lines and contact pads and then covered with the electrochromic material 2, which is patterned to give pixels, which may be individually addressed through the tin oxide lines.

These devices are especially applicable as a variable reflectivity mirror and/or imparting readable information. A further modification can be made in which the porous layer 3 has incorporated into it a coloured dye, such as phenol red. In such a case the sol/gel derived layer might only be fired at about 120°C in order to protect the incorporated organic dye. The optical contrast would then not be silver/blue (of a reflector system) but rather reflected red/black (black writing on red background). Other colour combinations are possible as a result of modifying the porous layer 3.

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CLAIMS

1. An electrochromic display device comprising, in order:

(1) a layer of a transparent electrically conductive material;

(2) a layer of an electrochromic material which changes colour when atoms resulting from electrolysis of water are dissolved in it;

(3) a layer which acts as a source of water; and

(4) a layer of a reflecting electronic conductor,

characterised in that the layer (3) is of an insulating transparent material having interconnected pores which are such that they spontaneously become moist on exposure to humidity, and further characterised in that the layer (4) is sufficiently porous to allow access of water vapour to the layer (3).

2. An electrochromic display device according to Claim 1, wherein the layer (4) is porous metal.

3. An electrochromic display device according to Claim 2, wherein the metal is silver, chromium or aluminium.

4. An electrochromic display device according to any preceding claim, wherein the layer (3) is an insulating oxide.

5. An electrochromic display device according to any preceding claim, wherein the layer (3) has pores 3-50Å across.

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The Patent Office

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Claims searched: 1 to 5

Examiner: Mr. G.M.Pitchman
Date of search: 21 March 1995

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.N): G2F(FCL)

Int Cl (Ed.6): G02F 1/153

Other: ONLINE:EDOC WPI JAPIO

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	US 5,216,536 (AGRAWAL)-see column 3 lines 40 to 57 and column 5 line 38 to column 6 line 26	1
X	Patent Abstracts of Japan Section P:P-939 Vol. 13 No.438 page 119 &JP1167735(MATSUSHITA)	1
X	WPI Abstract Accession No.86-322535/49 & JP61239227(CANON)	1,4
X	WPI Abstract Accession No.86-322531/49 & JP61239223(CANON)	1,4

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

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